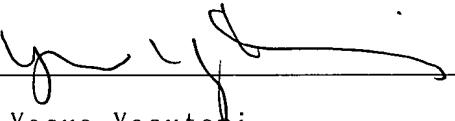


VERIFICATION OF TRANSLATION

I, Yasuo Yasutomi of Chuo BLDG., 4-20, Nishinakajima 5-chome, Yodogawa-ku, Osaka-shi, Osaka 532-0011 JAPAN, hereby declare that I am conversant with the Japanese and English languages and that I am the translator of the documents attached and certify that to the best of my knowledge and belief the following is a true and correct English translation of the Japanese Patent Application No. Hei 10-207328 in the name of KANEKA CORPORATION.

Dated this 6th day of August, 2004



Yasuo Yasutomi

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[To] Commissioner, Patent Office

[IPC] C08F 20/18

[Title of the Invention] POLYMER AND USE

[Number of Claims] 32

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[Indication of Fee]

[Number of Deposit Ledger] 005027

[The Amount of Payment] 21,000 yen

[List of Attached Documents]

[Document Name] Description 1

[Document Name] Abstract 1

[Necessity of Proof]

Needed

[Document Name] Description

[Title of the Invention] POLYMER AND USE

[Scope of Claims for Patent]

5 [Claim 1] A block copolymer which is produced by adding a polymer (I) containing a group represented by the general formula 1:



(wherein R^1 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms) in at least one terminus to 10 a living radical polymerization system.

[Claim 2] The block copolymer according to Claim 1, wherein, in the general formula 1, R^1 is a hydrogen atom.

[Claim 3] The polymer according to Claim 1 or 2, wherein the polymer (I) is a styrenic polymer.

15 [Claim 4] The polymer according to any of Claims 1 to 3, wherein the polymer (I) is a (meth)acrylic polymer.

[Claim 5] The polymer according to any of Claims 1 to 4, wherein the polymer (I) has a glass transition point of not lower than 25°C.

20 [Claim 6] The polymer according to any of Claims 1 to 5, wherein the polymer (I) has only one group represented by the general formula 1.

[Claim 7] The polymer according to any of Claims 1 to 6, wherein the polymer (I) has the number average molecular weight 25 of 500 to 100000.

[Claim 8] The polymer according to any of Claims 1 to 7, wherein the polymer (I) has the ratio between the weight average molecular weight (M_w) and the number average molecular weight (M_n) (M_w/M_n) as determined by gel permeation chromatography of 30 not more than 1.8.

[Claim 9] The polymer according to any of Claims 1 to 8, wherein the polymer (I) is produced by controlled radical polymerization.

35 [Claim 10] The polymer according to Claim 9, wherein the polymer (I) comprises a vinyl polymer produced by living radical

polymerization.

[Claim 11] The polymer according to Claim 10, wherein the polymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 7, 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst.

[Claim 12] The polymer according to Claim 11, wherein the metal complex to serve as a catalyst for producing the polymer (I) is a copper, nickel, ruthenium or iron complex.

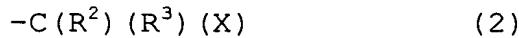
[Claim 13] The polymer according to Claim 12, wherein the metal complex to serve as a catalyst for producing the polymer (I) is a copper complex.

[Claim 14] The polymer according to Claim 9, wherein the polymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using a chain transfer agent.

[Claim 15] The polymer according to any of Claims 10 to 13, wherein the polymer (I) is produced by using an alkenyl-containing organic halide or a sulfonyl halide as an initiator.

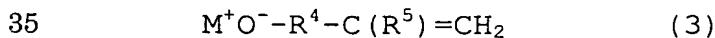
[Claim 16] The polymer according to Claim 15, wherein the polymer (I) is produced by using an allyl halide as an initiator.

[Claim 17] The polymer according to any of Claims 1 to 16, wherein the polymer (I) is produced by converting a halogen group of a vinyl polymer having a terminal structure represented by the general formula 2:



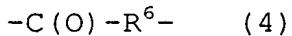
(wherein R^2 and R^3 may be the same or different and each represents a group bound to an ethylenic unsaturated group of a vinyl monomer; X represents chlorine, bromine or iodine) to an alkenyl-containing substituent.

[Claim 18] The polymer according to Claim 17, wherein the polymer (I) is produced by substituting an alkenyl-containing oxy anion represented by the general formula 3:



(wherein R^4 represents a divalent organic group containing 1 to 20 carbon atoms which may optionally contain one or more ether bonds or ester bonds; R^5 represents hydrogen, an alkyl group containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms, or an aralkyl group containing 7 to 10 carbon atoms; M^+ represents an alkali metal ion or quaternary ammonium ion) for the terminal halogen in the general formula 2.

[Claim 19] The production method according to Claim 18, wherein R^4 in the general formula 3 is a divalent organic group represented by the following general formula 4:

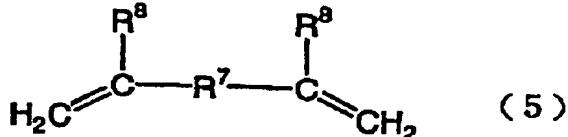


(wherein R^6 represents a direct bond, or a divalent organic group containing 1 to 19 carbon atoms which may optionally contain one or more ether bonds or ester bonds).

[Claim 20] The polymer according to any of Claims 1 to 13, wherein the polymer (I) is produced by adding a compound represented by the general formula (5):

[Chemical 1]

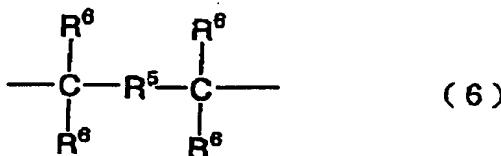
20



(wherein R^7 represents an alkyl group containing 1 to 20 carbon atoms, or a group having a structure represented by the general formula 6:

[Chemical 2]

30

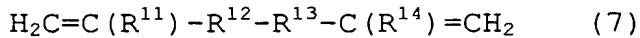


(wherein R^9 represents an oxygen atom, nitrogen atom or organic group containing 1 to 20 carbon atoms; R^{10} may be the same or different and represents a hydrogen atom or a methyl group) and R^8 represents a hydrogen atom or a methyl group}

during or after completion of living radical polymerization.

[Claim 21] The polymer according to any of Claims 1 to 13, wherein the polymer (I) is produced by adding a compound having both an alkenyl group with high polymerizability and an alkenyl group with low polymerizability during or after completion of the living radical polymerization.

[Claim 22] The polymer according to Claim 21, wherein the compound having both an alkenyl group with high polymerizability and an alkenyl group with low polymerizability is represented by the general formula 7:



(wherein R^{11} and R^{14} represent hydrogen or a methyl group, R^{12} represents $-\text{C}(\text{O})\text{O}-$ (ester group), or an ortho-, meta-, para-phenylene group, and R^{13} represents a direct bond or a divalent organic group containing 1 to 20 carbon atoms, which may optionally contain one or more ether bonds).

[Claim 23] The polymer according to any of Claims 1 to 22, wherein a polymer chain produced by living radical polymerization comprising adding the polymer (I) has a glass transition point not higher than 25°C.

[Claim 24] The polymer according to any of Claims 1 to 22, wherein the polymer produced by living radical polymerization comprising adding the polymer (I) is a styrene polymer.

[Claim 25] The polymer according to any of Claims 1 to 22, wherein the polymer produced by living radical polymerization comprising adding the polymer (I) is a (meth)acrylic polymer.

[Claim 26] The polymer according to any of Claims 1 to 25, wherein the living radical polymerization comprising adding the polymer (I) is a polymerization system polymerizing a vinyl monomer using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 7, 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst.

[Claim 27] The polymer according to Claim 26, wherein the metal complex to serve as a catalyst for the living radical

polymerization comprising adding the polymer (I) is a copper, nickel, ruthenium or iron complex.

[Claim 28] The polymer according to Claim 27, wherein the metal complex to serve as a catalyst for the living radical 5 polymerization comprising adding the polymer (I) is a copper complex.

[Claim 29] The polymer according to Claims 1 to 28, wherein the living radical polymerization comprising adding the polymer (I) is started from a di- or more functional initiator.

10 [Claim 30] The polymer according to any of Claims 1 to 29, wherein the ratio between the weight average molecular weight (M_w) and the number average molecular weight (M_n) (M_w/M_n) as determined by gel permeation chromatography of not more than 1.8.

15 [Claim 31] A thermoplastic elastomer which comprises, as the main component thereof, the polymer according to any of Claims 1 to 30.

20 [Claim 32] An impact resistance improving agent which comprises, as the main component thereof, the polymer according to any of Claims 1 to 30.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

25 The present invention relates to a method for producing a block copolymer which comprises adding an alkenyl-terminated polymer to a living radical polymerization system, the polymer, and its use.

[0002]

[Prior Art]

30 Block copolymers composed of different polymer block species bound to each other are generally produced by polymerizing different monomer species in succession. Heretofore, various methods of polymerization have been developed and attempts have been made to produce block 35 copolymers using them. When cationic polymerization is

employed, however, it is difficult to control the polymerization, since the growing species carbenium ion is unstable. In recent years, examples of the so-called living cation polymerization in which the growing carbenium ion in the 5 cationic polymerization is inhibited from undergoing isomerization, chain transfer reaction or termination reaction have been reported. For example, Higashimura et al. (Macromolecules, 17, 265, 1984) report that cationic living polymerization is possible in vinyl ether polymerization using 10 a combination of hydrogen iodide and iodine as an initiator. However, the polymerization using such initiator has various problems; for instance, its application is restricted to those monomers which have an alkoxy group high in electron donating ability and are highly susceptible to cationic polymerization, 15 and the initiator is unstable and difficult to handle.

[0003]

On the other hand, Kennedy et al. (Japanese Kokai Publication Sho-62-48704, Japanese Kokai Publication Sho-64-62308), by polymerizing olefin monomers, such as 20 isobutylene, using an organic carboxylic acid or an ester, or an ether as an initiator in combination with a Lewis acid, showed that cationic living polymerization is possible with olefin monomers as well. This method has been modified in several ways, and Nippon Zeon (Japanese Kokoku Publication Hei-07-59601) has 25 succeeded in obtaining block copolymers by successive monomer addition with additional use of an amine. In this modification, isobutylene-based block copolymers comprising an isobutylene polymer and a styrene polymer are produced in a mixed solvent composed of methylene chloride and hexane. However, such 30 halogenated hydrocarbons containing 1 or 2 carbon atoms have problems; for instance, they are difficult to handle, and require large scale equipment for preventing them from being discharged into the environment to raise the cost of production. Although, on the other hand, such polymerization is also 35 possible in a halogen-free solvent such as toluene, very fine

adjustment is required, depending on the monomer, for the monomer to show adequate polarity. It is thus very difficult to establish the conditions for successive polymerization of two or more monomer species differing in reactivity.

5 [0004]

Meanwhile, in recent years, controlled radical polymerization techniques and, further, living radical polymerization techniques have been developed, making it possible to well control the living polymerization.

10 Matyjaszewski et al. report a method of synthesizing block copolymers by successively adding monomers using the atom transfer radical polymerization technique to be mentioned later herein or by using a macro-initiator. These techniques, however, may sometimes encounter problems; successive 15 polymerization of monomers is difficult since respective monomers require different optimum polymerization conditions, or it is difficult to introduce, terminally into the macro-initiator, an initiator terminus optimal to the next monomer to be polymerized.

20 [0005]

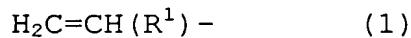
[Subject which the Invention is to Solve]

The present invention has for its object to provide a method for easily producing a block copolymer composed of any of various polymers and a living radical polymerization polymer 25 without requiring optimization of polymerization conditions which is difficult to achieve.

[0005]

[Means for Solving the Problems]

The present invention relates to a block copolymer which 30 is produced by adding a polymer (I) containing a group represented by the general formula 1:



(wherein R^1 represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms) in at least one terminus to 35 a living radical polymerization system.

[0007]

The polymer (I) is preferably polymerized by controlled radical polymerization, more preferably by living radical polymerization, and particularly preferably by atom transfer radical polymerization. The terminal group is introduced by the initiator and various functional group conversions. The polymer (I) also has a characteristic for having a narrow molecular weight distribution.

The living radical polymerization for adding the polymer (I) is not particularly restricted, but preferred is the atom transfer radical polymerization.

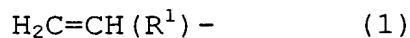
[0008]

The block copolymer of the present invention is useful as a thermoplastic elastomer or an impact resistance improving agent.

[0009]

[Embodiment of the Invention]

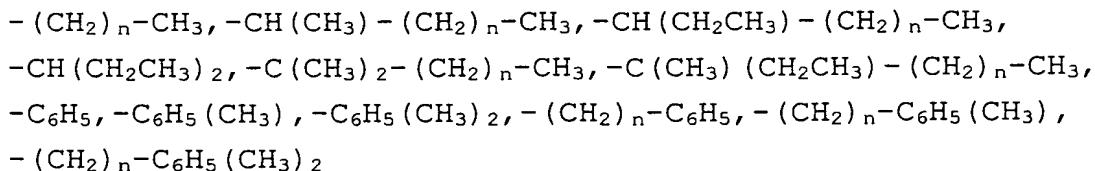
The present invention relates to a block copolymer which is produced by adding the polymer (I) containing a group represented by the general formula 1:



in at least one terminus to a living radical polymerization system.

[0010]

In the general formula 1, R^1 is a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, specifically including, for example, the following groups:



(wherein n is an integer not smaller than 0 and the total number of carbon atoms in each group is not greater than 20). Among these, a hydrogen atom is preferred.

[0011]

The number of groups represented by the general formula 1 in polymer (I) is not particularly restricted but may be selected depending on the structure of the desired block copolymer. Thus, said polymer may have one, two or more alkenyl 5 groups.

<Monomer >

The main chain of the polymer (I) of the present invention is not restricted, but preferably a vinyl polymer. The vinyl monomer constituting the polymer is not particularly restricted 10 and various ones may be used. Examples are (meth)acrylic monomers such as (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, γ -(methacryloyloxypropyl)trimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylmethylethyl (meth)acrylate, 2-perfluoroethylmethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, 35 α -methylstyrene, chlorostyrene, styrenesulfonic acid and

salts thereof; fluorine-containing vinyl monomers such as perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing vinyl monomers such as vinyltrimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and dialkyl esters; maleimide monomers such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile group-containing vinyl monomers such as acrylonitrile and methacrylonitrile; amide group-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol and so on. These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of the products. More preferred are acrylic acid ester monomers and methacrylic acid ester monomers, and still more preferred are butyl acrylate monomers. In the practice of the present invention, such a preferred monomer may be copolymerized with some other monomers and, on that occasion, the content of such preferred monomer is preferably 40% on the weight basis. The term (meth)acrylic acid employed hereinabove means acrylic acid and/or methacrylic acid.

30 [0012]

The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the polymer (I) of the present invention is not particularly restricted but is preferably not more than 1.8, more preferably

not more than 1.6, and most preferably not more than 1.3.

The number average molecular weight of the polymer (I) of the present invention is not particularly restricted but is preferably within the range of 500 to 1,000,000, more preferably 5 within the range of 3,000 to 40,000.

The glass transition point of the polymer (I) is preferably not lower than 25°C in view of physical properties of the product block copolymer and the like.

<Method of producing the polymer (I)>

10 The method of producing the polymer (I) is not particularly restricted but said polymer is preferably produced by controlled radical polymerization. As the controlled radical polymerization, there may be mentioned polymerization which comprises using a chain transfer agent, or living radical 15 polymerization which has been recently developed. The latter is preferable from the polymerization controllability point of view.

[0013]

20 The method of introducing the group represented by the general formula 1 to the terminus of the polymer (I) is not particularly restricted, but there may be mentioned a method comprising carrying out living radical polymerization using an initiator containing the group represented by the general formula 1, a production method comprising converting a halogen 25 group of a vinyl polymer having the terminal structure represented by the general formula 2:



(wherein R² and R³ may be the same or different and each represents a monovalent organic group derived from a group bound 30 to an ethylenic unsaturated group of a vinyl monomer; X represents chlorine, bromine or iodine) which is produced by a polymerization using a chain transfer agent, living radical polymerization, or the like with an alkenyl-containing substituent, and a method comprising adding a group which is, 35 in the living radical polymerization system, capable of

reacting with the growing terminus, and a compound having the group represented by the general formula 1.

[0014]

As the polymerization which comprises using a chain transfer agent for producing the polymer containing the general formula 2 at a terminus, there may be mentioned a polymerization comprising using a halide as a chain transfer agent (telogen). As the halide, carbon tetrachloride, carbon tetrabromide, methylene chloride, methylene bromide or the like may be used.

10 <Living radical polymerization>

In its narrow sense, the term "living polymerization" means that polymerization in which the molecular chain grows while a terminus always retain activity. Generally, however, it also includes, within the meaning thereof, pseudoliving polymerization in which molecules grow while terminally inactivated molecules and terminally activated ones are in equilibrium. The latter definition is to be applied to the present invention. "Living radical polymerization" has recently been aggressively investigated by a number of groups.

20 As examples, there may be mentioned, among others, the method which uses cobalt porphyrin complex (Journal of the American Chemical Society, 1994, vol. 116, page 7943), the method which uses a radical capping agent, for example a nitroxide compound (Macromolecules, 1994, vol. 27, page 7228), and atom transfer radical polymerization (ATRP) in which an organic halide, for instance, is used as an initiator and a transition metal complex as a catalyst. The living radical polymerization hardly undergo termination reaction and give polymers narrow in molecular weight distribution (M_w/M_n being about 1.1 to 1.5)

25 and the molecular weight can arbitrarily be controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization regarded as difficult to control because of a high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other,

30 among others.

[0015]

"Living radical polymerization methods", which enable introduction of a specific functional group-containing monomer into a polymer at a substantially arbitrary site thereof in 5 addition to obtaining polymers with a narrow molecular weight distribution and a low viscosity on its properties, are more preferred as methods of producing the specific functional group-containing vinyl polymers.

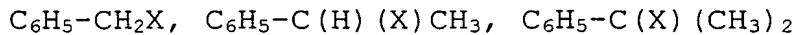
Among such "living radical polymerization methods", the 10 "atom transfer polymerization methods" for polymerizing vinyl monomers using an organic halide, sulfonyl halide or the like as an initiator and a transition metal complex as a catalyst (for example, refer to Matyjaszewski et al., the Journal of the American Chemical Society, 1995, vol. 117, page 5614; 15 Macromolecules, 1995, vol. 28, page 7901; Science, 1996, vol. 272, page 866; or Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721) are more preferred as the method of producing specific functional group-containing vinyl polymers, since, in addition to the characteristic features of the above-mentioned 20 "living radical polymerization methods", halogen, etc., relatively favorable for functional group conversion reactions is contained at its terminus and the degree of freedom is high in designing the initiator or catalyst. Also in the method of the present invention, the atom transfer polymerization method 25 is preferred.

[0016]

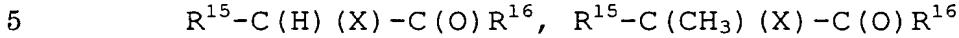
In this atom transfer radical polymerization, an organic halide, in particular an organic halide having a highly reactive carbon-halogen bond (e.g. a carbonyl compound having a halogen 30 in α -position or a compound having a halogen at the benzyl site), or a sulfonyl halide compound is used as an initiator.

<Initiator of atom transfer radical polymerization>

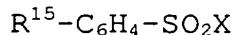
The organic halide or a sulfonyl halide compound used in the atom transfer radical polymerization specifically include, 35 among others:



(in the above chemical formulas, C_6H_5 is a phenyl group and X is chlorine, bromine or iodine);



(in which R^{15} represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 carbon atoms or an aralkyl group having 7 to 20 carbon atoms, X is chlorine, bromine or iodine, and R^{16} represents a monovalent organic group having 1 to 20 carbon atoms); and



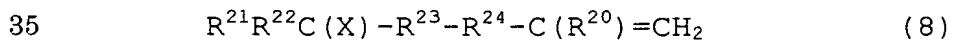
(in which R^{15} is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or aralkyl group having 7 to 20 carbon atoms and X is chlorine, bromine or iodine).

[0017]

Furthermore, when an organic halide or sulfonyl halide having a functional group other than the functional group for initiating polymerization is used as the initiator, a polymer 20 introduced with a functional group at its terminus can be easily obtained. As such functional group, there may be mentioned alkenyl, hydroxyl, epoxy, amino, amide and silyl groups, among others. By introducing the group represented by the general formula 1 to the polymer produced from an initiator containing 25 such functional group by various methods described later to produce the polymer (I), and adding the polymer to the living radical polymerization system, a block copolymer containing carious functional group at its terminus can be easily obtained.

[0018]

30 When an alkenyl-containing initiator is used, the polymer (I) containing the group represented by the general formula 1 can be easily obtained. The alkenyl-containing organic halide is not restricted but may be one having the structure shown by the general formula 8:



(wherein R^{20} is a hydrogen atom or a methyl group, R^{21} and R^{22} each is a hydrogen atom or a monovalent alkyl having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group and R^{21} and R^{22} may be bound to each other at 5 respective other termini, R^{23} is $-C(O)O-$ (ester group), $-C(O)-$ (keto group) or an o-, m- or p-phenylene group, R^{24} is a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally contain one or more ether bonds, and X is chlorine, bromine or iodine).

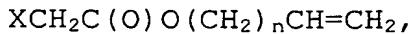
10 In these compounds, carbon to which a halogen is bound is bound to a carbonyl or phenyl group, thereby polymerization is started after the carbon-halogen bond is activated.

[0019]

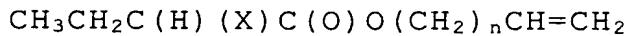
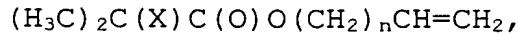
15 As specific examples of the substituents R^{21} and R^{22} , there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, etc. R^{21} and R^{22} may be bound to each other at respective other termini to form a cyclic skeleton. In such case, $-R^{21}-R^{22}-$ may be, for example, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2CH_2-$ and the like.

20 [0020]

As specific examples of the alkenyl-containing organic halide represented by the general formula 8, there may be mentioned the following:



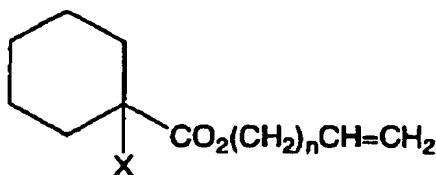
25 $H_3CC(H)(X)C(O)O(CH_2)_nCH=CH_2$,



[0021]

[Chemical 3]

30



[0022]

35 (in the above formulas, X is chlorine, bromine or iodine and

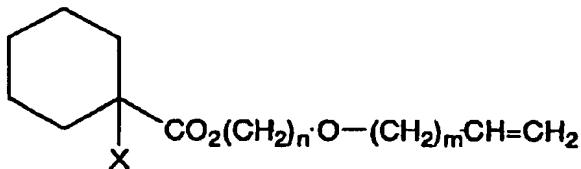
n is an integer of 0 to 20);

XCH₂C(O)O(CH₂)_nO(CH₂)_mCH=CH₂,
 H₃CC(H)(X)C(O)O(CH₂)_nO(CH₂)_mCH=CH₂,
 (H₃C)₂C(X)C(O)O(CH₂)_nO(CH₂)_mCH=CH₂,

5 CH₃CH₂C(H)(X)C(O)O(CH₂)_nO(CH₂)_mCH=CH₂,
 [0023]

[Chemical 4]

10



[0024]

(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

15

o, m, p-XCH₂-C₆H₄-(CH₂)_n-CH=CH₂,
 o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)_n-CH=CH₂,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)_n-CH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);

20

o, m, p-XCH₂-C₆H₄-(CH₂)_n-O-(CH₂)_m-CH=CH₂,
 o, m, p-CH₃C(H)(X)-C₆H₄-(CH₂)_n-O-(CH₂)_m-CH=CH₂,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-(CH₂)_n-O-(CH₂)_mCH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

25

o, m, p-XCH₂-C₆H₄-O-(CH₂)_n-CH=CH₂,
 o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)_n-CH=CH₂,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)_n-CH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);

30

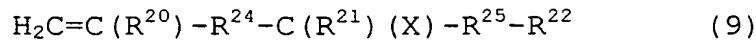
o, m, p-XCH₂-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂,
 o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)_n-O-(CH₂)_m-CH=CH₂,

(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20 and m is an integer of 0 to 20).

35

As the alkenyl-containing organic halide, there may

further be mentioned compounds represented by the general formula 9:



(wherein R^{20} , R^{21} , R^{22} , R^{24} and X are defined above and R^{25} is a direct bond, $-\text{C}(\text{O})\text{O}-$ (ester group), $-\text{C}(\text{O})-$ (keto group) or an $\text{o}-$, $\text{m}-$ or $\text{p}-$ phenylene group).

R^{24} is a direct bond or a divalent organic group having 1 to 20 carbon atoms (which may contain one or more ether bonds) and, when it is a direct bond, the vinyl group is bound to the carbon to which the halogen is bound, to form an allyl halide. In this case, the carbon-halogen bond is activated by the neighboring vinyl group, so that it is not always necessary for R^{25} to be a $\text{C}(\text{O})\text{O}$ group or a phenylene group, for instance, but it may be a direct bond. When R^{24} is not a direct bond, R^{25} is preferably a $\text{C}(\text{O})\text{O}$ group, $\text{C}(\text{O})$ group or phenylene group so that the carbon-halogen bond may be activated.

[0025]

As a specific example of compounds represented by the general formula 9, there can be mentioned,

20 $\text{CH}_2=\text{CHCH}_2\text{X}$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{X}$,
 $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}_3$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{H})(\text{X})\text{CH}_3$,
 $\text{CH}_2=\text{CHC}(\text{X})(\text{CH}_3)_2$, $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{C}_2\text{H}_5$,
 $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}(\text{CH}_3)_2$,
 $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{C}_6\text{H}_5$, $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}_2\text{C}_6\text{H}_5$,
25 $\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$,
 $\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
30 $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$,
(in the above formulas, X is chlorine, bromine or iodine, and R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 35 20 carbon atoms). Among these, allyl chloride and allyl bromide

are preferred from cost and availability viewpoint.

[0026]

Specific examples of the alkenyl-containing sulfonyl halide are as follows:

5 o-, m- or p-CH₂=CH-(CH₂)_n-C₆H₄-SO₂X and

o-, m- or p-CH₂=CH-(CH₂)_n-O-C₆H₄-SO₂X

(wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20), among others.

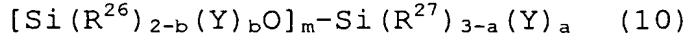
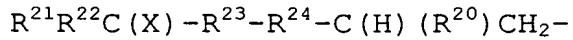
[0027]

10 When an alkenyl-containing initiator is used, care should be taken since there is a possibility that olefin of the initiator may also react with the polymerization terminus.

15 Additionally, a polymer produced by using the alkenyl-containing initiator by itself becomes the polymer (I), but also has a growing terminus. The growing terminus may become not only a growing terminus of radical polymerization, but also an initiator of living radical polymerization in which the polymer (I) is added. In this case, there may occur undesirable polymerization reaction other than the bond of the 20 polymers, which the present invention intends to. For avoiding this reaction, the growing terminus (in many cases, a halogen group) may be removed by an alkaline treatment, and the like.

[0028]

25 The crosslinking silyl-containing organic halide is not particularly restricted but includes, among others, those having a structure shown by the general formula 10:



30 (wherein R²⁰, R²¹, R²², R²³, R²⁴ and X are as defined above, R²⁶ and R²⁷ each is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms, or a triorganosiloxy group represented by (R')₃SiO- (in which R' is a monovalent hydrocarbon group having 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R²⁶ and/or

R^{27} groups, they may be the same or different, Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different, a represents 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0 to 19, provided that the relation $a + mb \geq 1$ should be satisfied.

As a specific example of compounds represented by the general formula 10, there can be mentioned,

$XCH_2C(O)O(CH_2)_nSi(OCH_3)_3$, $CH_3C(H)(X)C(O)O(CH_2)_nSi(OCH_3)_3$,
 $(CH_3)_2C(X)C(O)O(CH_2)_nSi(OCH_3)_3$, $XCH_2C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$,

10 $CH_3C(H)(X)C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$,
 $(CH_3)_2C(X)C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$,
(wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20),
 $XCH_2C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$,

15 $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$,
 $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$,
 $CH_3CH_2C(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$,
 $XCH_2C(O)O(CH_2)_nO(CH_2)_mSi(CH_3)(OCH_3)_2$,
 $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_m-Si(CH_3)(OCH_3)_2$,

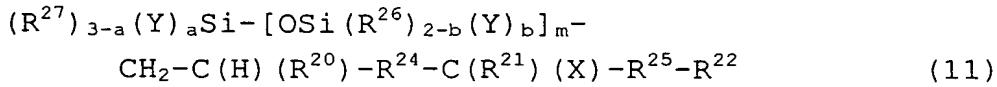
20 $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_m-Si(CH_3)(OCH_3)_2$,
 $CH_3CH_2C(H)(X)C(O)O(CH_2)_nO(CH_2)_m-Si(CH_3)(OCH_3)_2$,
(wherein, in each formula, X is chlorine, bromine or iodine, n is an integer of 0 to 20, and m is an integer of 0 to 20),
 $o, m, p-XCH_2-C_6H_4-(CH_2)_2Si(OCH_3)_3$,

25 $o, m, p-CH_3C(H)(X)-C_6H_4-(CH_2)_2Si(OCH_3)_3$,
 $o, m, p-CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_2Si(OCH_3)_3$,
 $o, m, p-XCH_2-C_6H_4-(CH_2)_3Si(OCH_3)_3$,
 $o, m, p-CH_3C(H)(X)-C_6H_4-(CH_2)_3Si(OCH_3)_3$,
 $o, m, p-CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_3Si(OCH_3)_3$,

30 $o, m, p-XCH_2-C_6H_4-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$,
 $o, m, p-CH_3C(H)(X)-C_6H_4-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$,
 $o, m, p-CH_3CH_2C(H)(X)-C_6H_4-(CH_2)_2-O-(CH_2)_3Si(OCH_3)_3$,
 $o, m, p-XCH_2-C_6H_4-O-(CH_2)_3Si(OCH_3)_3$,
 $o, m, p-CH_3C(H)(X)-C_6H_4-O-(CH_2)_3Si(OCH_3)_3$,
35 $o, m, p-CH_3CH_2C(H)(X)-C_6H_4-O-(CH_2)_3-Si(OCH_3)_3$,

o, m, p-XCH₂-C₆H₄-O-(CH₂)₂-O-(CH₂)₃-Si(OCH₃)₃,
 o, m, p-CH₃C(H)(X)-C₆H₄-O-(CH₂)₂-O-(CH₂)₃-Si(OCH₃)₃,
 o, m, p-CH₃CH₂C(H)(X)-C₆H₄-O-(CH₂)₂-O-(CH₂)₃-Si(OCH₃)₃,
 (wherein, in each formula, X is chlorine, bromine or iodine).

5 As further examples of the crosslinking silyl-containing organic halide, there may be mentioned those having a structure represented by the general formula 11:



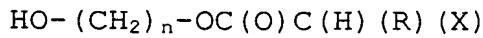
10 (wherein R²⁰, R²¹, R²², R²⁴, R²⁵, R²⁶, R²⁷, a, b, m, X and Y are as defined above).

As a specific example of such compounds, there can be mentioned;

(CH₃O)₃SiCH₂CH₂C(H)(X)C₆H₅, (CH₃O)₂(CH₃)SiCH₂CH₂C(H)(X)C₆H₅,
 15 (CH₃O)₃Si(CH₂)₂C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₂C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₄C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₉C(H)(X)-CO₂R, (CH₃O)₂(CH₃)Si(CH₂)₉C(H)(X)-CO₂R,
 (CH₃O)₃Si(CH₂)₃C(H)(X)-C₆H₅, (CH₃O)₂(CH₃)Si(CH₂)₃C(H)(X)-C₆H₅,
 20 (CH₃O)₃Si(CH₂)₄C(H)(X)-C₆H₅, (CH₃O)₂(CH₃)Si(CH₂)₄C(H)(X)-C₆H₅,
 (wherein, in each formula, X is chlorine, bromine or iodine, R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms.), and the like.

25 [0029]

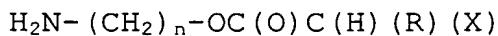
The hydroxyl-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:



30 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The amino-containing organic halide or sulfonyl halide
 35 is not particularly restricted but includes compounds

represented by the following formula:

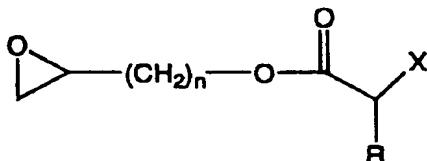


(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl having 5 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The above-mentioned epoxy-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

10 [0030]

[Chemical 5]



15

[0031]

(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

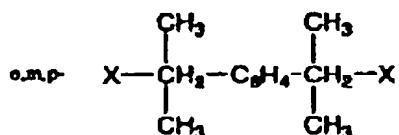
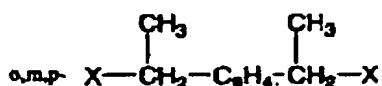
For obtaining polymers having two or more terminal structures represented by the general formula 2 within each molecule, an organic halide or sulfonyl halide having two or more initiation sites is used. Specific examples are:

25 [0032]

[Chemical 6]

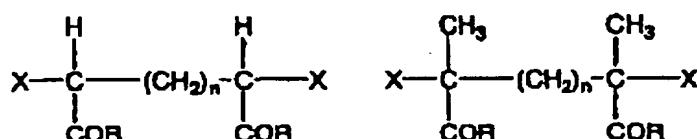
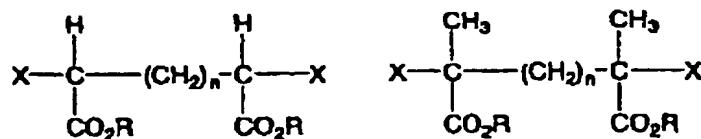


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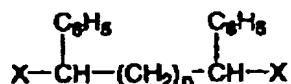
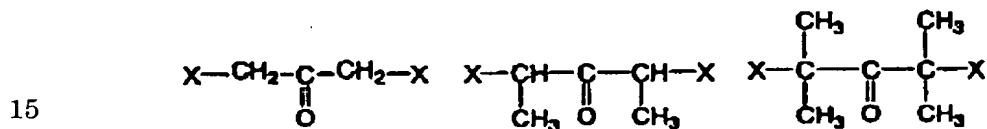


(in which C₆H₄ represents a phenylene group and X is chlorine, bromine or iodine);

35



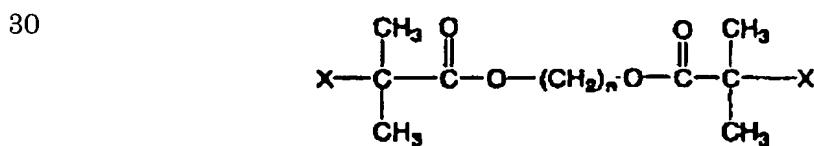
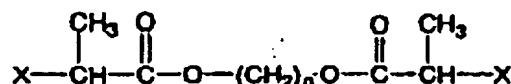
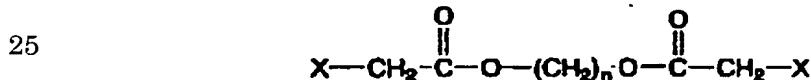
10 (in which R is an alkyl group having 1 to 20 carbon atoms, aryl or aralkyl group, n is an integer of 0 to 20 and X is chlorine, bromine or iodine);



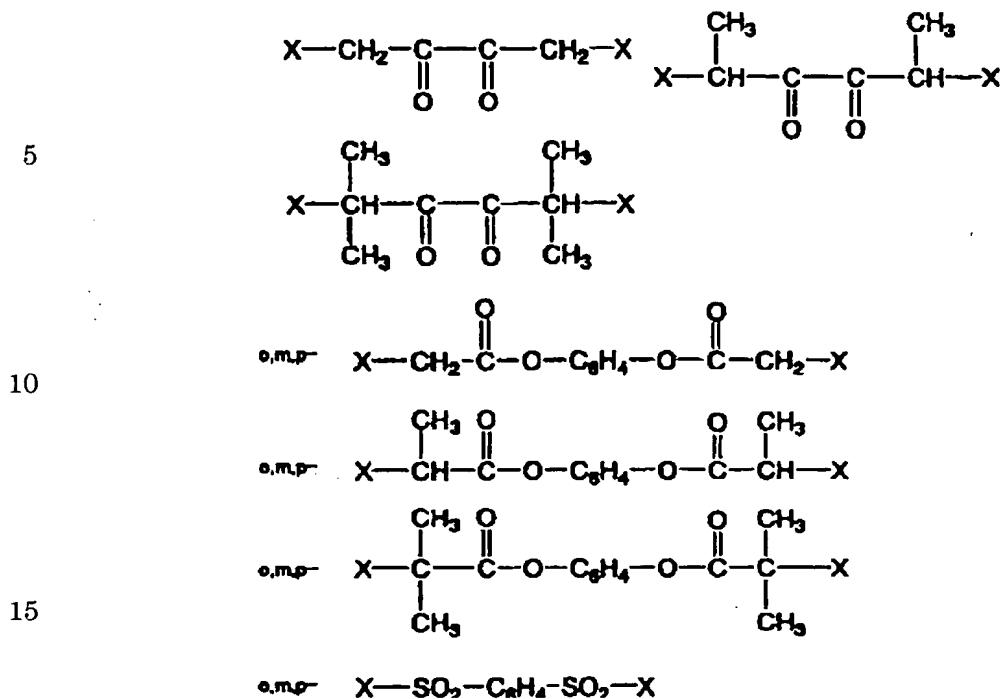
20 (in which X is chlorine, bromine or iodine and n is an integer of 0 to 20);

[0033]

[Chemical 7]



35 (in which n is an integer of 0 to 20 and X is chlorine, bromine or iodine);



(in which X is chlorine, bromine or iodine), and the like.

20 [0034]

<Monomer of controlled radical polymerization>

The vinyl monomer to be used in controlled radical polymerization of the present invention is not particularly restricted and those mentioned above may be used.

25 <Catalyst of atom radical polymerization>

The transition metal complex to be used as a polymerization catalyst for the atom transfer radical polymerization is not particularly restricted but preferably is a metal complex containing an element of the group 7, 8, 9, 30 10 or 11 of the periodic table as a central metal, and more preferably are complexes of monovalent copper, copper (valence: zero), divalent ruthenium, divalent iron or divalent nickel. Among them, copper complexes are preferred in view of cost and reaction controllability. Specific examples of monovalent 35 copper compounds are cuprous chloride, cuprous bromide, cuprous

iodide, cuprous cyanide, cuprous oxide, cuprous perchlorate and the like. When a copper compound is used, a ligand, such as 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or a derivative thereof or a polyamine such as

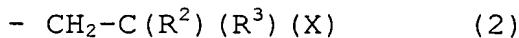
5 tetramethylethylenetriamine (TMEDA),
pentamethyldiethylenetriamine or hexamethyl
(2-aminoethyl)amine, is added to enhance the catalytic activity.
A tristriphenylphosphine complex of divalent ruthenium
chloride ($\text{RuCl}_2(\text{PPh}_3)_3$) is also suited for use as a catalyst.
10 When a ruthenium compound is used as a catalyst, an aluminum
alkoxide is added as an activator. Furthermore, a
bistriphenylphosphine complex of divalent iron ($\text{FeCl}_2(\text{PPh}_3)_2$),
a bistriphenylphosphine complex of divalent nickel
($\text{NiCl}_2(\text{PPh}_3)_2$) and a bistritylphosphine complex of divalent
15 nickel ($\text{NiBr}_2(\text{PBu}_3)_2$) are also suited as a catalysts.

<Solvent and temperature of controlled radical polymerization>

The above-mentioned controlled radical polymerization, living radical polymerization, and atom transfer radical polymerization can be carried out in the absence or presence
20 of various solvents. As the solvent, there may be mentioned, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl
25 ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and tert-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; and carbonate solvents such as
30 ethylene carbonate and propylene carbonate. These may be used singly or two or more of them may be used in admixture. The above polymerization can be conducted within the temperature range of room temperature to 200°C, preferably 50°C to 150°C.
<Terminus conversion method>

35 The polymer (I) containing the group represented by the

general formula 1 can also be produced by converting a halogen group of the thus obtained vinyl polymer having the terminal structure represented by the general formula 2:

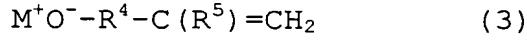


5 (wherein R^2 and R^3 may be the same or different and each represents a monovalent organic group derived from a group bound to a vinyl group of a vinyl monomer; X represents chlorine, bromine or iodine) to an alkenyl-containing substituent.
[0035]

10 The converting method is not particularly restricted, but there may be mentioned the following method.

<Oxy anion substitution>

The polymer (I) is produced by substituting an alkenyl-containing oxy anion represented by the general formula 15 3:

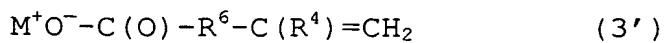


(wherein R^4 represents a divalent organic group containing 1 to 20 carbon atoms which may optionally contain one or more ether bonds or ester bonds; R^5 represents hydrogen, an alkyl group 20 containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms, or an aralkyl group containing 7 to 10 carbon atoms; M^+ represents an alkali metal ion or quaternary ammonium ion) for the terminal halogen in the general formula 2.

In the following, the substitution method using an 25 alkenyl-containing oxy anion is described in detail.

[0036]

In the general formula 3, which represents the alkenyl-containing oxy anion, R^4 and R^5 are the same substituent as defined above. As specific examples of these, all of those 30 mentioned above may be used. Particularly, when R^4 is represented by $-\text{C}(\text{O})-\text{R}^6-$, the above general formula 3 is represented by the general formula 3'.



In the above general formula 3, M^+ is a counter cation 35 of an oxy anion, and represents an alkali metal ion or quaternary

ammonium ion. As the above alkali metal ion, there may be mentioned lithium ion, sodium ion and potassium ion and, sodium ion or potassium ion is preferable. As the quaternary ammonium ion, there may be mentioned tetramethylammonium ion,
 5 tetraethylammonium ion, trimethylbenzylammonium ion, trimethyldodecylammonium ion and tetrabutylammonium ion, dimethyl piperidinium ion, among others.

[0037]

As example of the precursor of the alkenyl-containing oxy anion represented by the general formula 3, there may be mentioned the following:

$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{OH}$, $\text{H}_2\text{C}=\text{CH}-\text{CH}(\text{CH}_3)-\text{OH}$, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}_2-\text{OH}$,
 $\text{H}_2\text{C}=\text{CH}- (\text{CH}_2)_n-\text{OH}$ (n represents an integer 2 to 20),
 $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}- (\text{CH}_2)_2-\text{OH}$, $\text{H}_2\text{C}=\text{CH}-\text{C}(\text{O})\text{O}- (\text{CH}_2)_2-\text{OH}$,
 15 $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}(\text{O})\text{O}- (\text{CH}_2)_2-\text{OH}$, o-, m-, p- $\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$,
 $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}_6\text{H}_4-\text{OH}$,
 $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{OH}$,
 $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$, $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$,
 $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{CH}_2-\text{OH}$ and the like.

20 [0038]

Furthermore, as example of the precursor of the alkenyl-containing oxy anion represented by the general formula 3, there may also be mentioned the following:

$\text{H}_2\text{C}=\text{CH}-\text{C}(\text{O})-\text{OH}$, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}(\text{O})-\text{OH}$, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}(\text{O})-\text{OH}$,
 25 $\text{H}_2\text{C}=\text{CH}- (\text{CH}_2)_n-\text{C}(\text{O})-\text{OH}$ (n represents an integer 2 to 20),
 $\text{H}_2\text{C}=\text{CH}- (\text{CH}_2)_n-\text{OC}(\text{O})- (\text{CH}_2)_m-\text{C}(\text{O})-\text{OH}$ (m and n are the same or different, each represents an integer of 0 to 19),
 $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$, $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$,
 $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$,
 30 $\text{o}-, \text{m}-, \text{p}-\text{H}_2\text{C}=\text{CH}- (\text{CH}_2)_n-\text{OC}(\text{O})-\text{C}_6\text{H}_4-\text{C}(\text{O})-\text{OH}$ (n represents an integer 0 to 13) and the like. These are the compounds which may also be represented by the above general formula 3'.

[0039]

The alkenyl-containing oxy anion represented by the
 35 general formula 3 may be prepared by reacting the

above-mentioned precursor and a base. As the base, various ones may be used. Examples thereof include sodium methoxide, potassium methoxide, lithium methoxide, sodium ethoxide, potassium ethoxide, lithium ethoxide, sodium tert-butoxide, 5 potassium tert-butoxide, sodium carbonate, potassium carbonate, lithium carbonate, sodium hydrogencarbonate, sodium hydroxide, potassium hydroxide, sodium hydride, potassium hydride, methylolithium, ethyllithium, n-butyllithium, tert-butyllithium, lithium diisopropylamide, 10 lithium hexamethyldisilazide; alkylamines such as trimethylamine, triethylamine and tributylamine; polyamines such as tetramethylethylenediamine and pentamethyldiethylenetriamine; pyridine compounds such as pyridine and picoline; and so forth. The base is used in 0.5 15 to 5 equivalent amount, preferably 0.8 to 1.2 equivalent amount, relative to the precursor.

[0040]

As the solvent to be used in reacting the above precursor with the base, there may be mentioned, among others, hydrocarbon 20 solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, 25 propanol, isopropanol, n-butyl alcohol and t-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; carbonate solvents such as ethylene carbonate and propylene carbonate; and amide solvents such as 30 dimethylformamide and dimethylacetamide. These may be used singly or two or more of them may be used in admixture.

[0041]

Specific production method of the alkenyl-containing oxy anion represented by the general formula 3 is further described 35 in detail. For example, when o-, m- or p- $H_2C=CH-CH_2-C_6H_4-OH$ is

used as the precursor, a base, for example potassium tert-butoxide, is charged into a reaction vessel in an inert gas atmosphere, and is suspended and dispersed in a solvent such as dimethyl acetoamide. To this dispersion solution, the above 5 allyl phenol is added in equivalent molar amount, and the mixture is subjected to reaction at room temperature to 70°C for 30 minutes to 1 hour, thereby an alkenyl-containing oxy anion in which potassium is substituted for an acidic proton can be obtained.

10 [0042]

The alkenyl-containing oxy anion in which M^+ is a quaternary ammonium ion can be obtained by directly reacting the above precursor with alkylamine or a pyridine compound. It can also be obtained by preparing one in which M^+ is a quaternary 15 ammonium ion and reacting this with a quaternary ammonium halide. Examples of the quaternary ammonium halide are tetramethylammonium halides, tetraethylammonium halides, trimethylbenzylammonium halides, trimethyldodecylammonium halides and tetrabutylammonium halides, among others.

20 [0043]

By reacting the alkenyl-containing oxy anion represented by the general formula 3 prepared by the above method with the vinyl polymer having the terminal structure represented by the general formula 2, the polymer (I) containing the group 25 represented by the general formula 1 at the main chain terminus can be obtained.

Herein, "a group bound to an ethylenic unsaturated group of a vinyl monomer" as used in the present invention is described.

30 [0044]

The vinyl monomer of the present invention is a compound represented by $CH_2=C(R^2)(R^3)$ (wherein R^2 and R^3 may be the same or different and each represents a monovalent organic group or a monovalent inorganic group such as a hydrogen atom), or a 35 compound such as maleic anhydride which contains a substituent

in a methylene group of the double bond. And the present invention comprises reacting the terminus of the polymer produced by polymerization reaction of a vinyl monomer to introduce an alkenyl group to the terminus.

5 [0045]

Accordingly, the site represented by $-\text{CH}_2(\text{R}^2)(\text{R}^3)-$ in the above general formula 2 is derived from a vinyl monomer, and therefore R^2 and R^3 can be said as "a group bound to an ethylenic unsaturated group of a vinyl monomer".

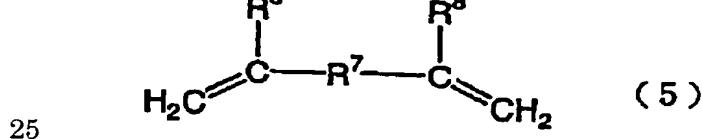
10 This reaction can be carried out in the fore-mentioned solvent at 0 to 150°C. The amount to be used of the alkenyl-containing oxy anion represented by the general formula 3 is 1 to 5 equivalent amount and preferably 1 to 1.2 equivalent amount relative to the terminal structure represented by the 15 general formula 2.

<Unconjugated diene>

The polymer (I) having the structure represented by the general formula 1 at the terminus is also produced by adding a compound represented by the general formula 5:

20 [0046]

[Chemical 8]

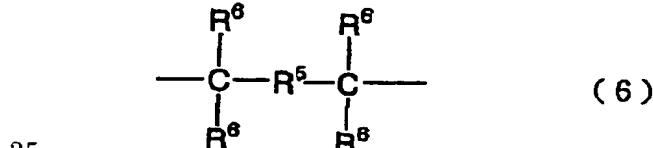


[0047]

{wherein R^7 represents an alkyl group containing 1 to 20 carbon atoms, or a group having a structure represented by the general formula 6:

30 [0048]

[Chemical 9]



[0049]

(wherein R^9 represents an oxygen atom, nitrogen atom or organic group containing 1 to 20 carbon atoms; R^{10} may be the same or different and represents a hydrogen atom or a methyl group) and R^8 represents a hydrogen atom or a methyl group} during or after completion of polymerization by various living radical polymerizations.

In the general formula 5, as specific examples of R^7 , there may be mentioned;

10 $-(CH_2)_n-$ (n is an integer of 1 to 20), $-CH(CH_3)-$, $-CH(CH_2CH_3)-$,
 $-C(CH_3)_2-$, $-C(CH_3)(CH_2CH_3)-$, $-C(CH_2CH_3)_2-$, $-CH_2CH(CH_3)-$,
 $-(CH_2)_n-O-CH_2-$ (n is an integer of 1 to 19), $-CH(CH_3)-O-CH_2-$,
 $-CH(CH_2CH_3)-O-CH_2-$, $-C(CH_3)_2-O-CH_2-$, $-C(CH_3)(CH_2CH_3)-O-CH_2-$,
 $-C(CH_2CH_3)_2-O-CH_2-$, $-(CH_2)_n-O-(CH_2)_m-$

15 (m and n are integers of 1 to 19, however, $2 \leq m + n \leq 20$),
 $-(CH_2)_n-C(O)O-(CH_2)_m-$
(m and n are integers of 1 to 19, however, $2 \leq m + n \leq 20$),
 $-(CH_2)_n-OC(O)-(CH_2)_m-C(O)O-(CH_2)_l-$
(l is an integer of 0 to 18, m and n are integers of 1 to 17,
20 however, $2 \leq l + m + n \leq 18$),
 $-(CH_2)_n-O-, m-$ or $p-C_6H_4-$, $-(CH_2)_n-O-, m-$, $p-C_6H_4-(CH_2)_m-$
(m is an integer of 0 to 13, n is an integer of 1 to 14, however,
 $1 \leq m + n \leq 14$),
 $-(CH_2)_n-O-, m-$ or $p-C_6H_4-O-(CH_2)_m-$

25 (m is an integer of 0 to 13, n is an integer of 1 to 14, however,
 $1 \leq m + n \leq 14$),
 $-(CH_2)_n-O-, m-$ or $p-C_6H_4-O-CH(CH_3)-$
(n is an integer of 1 to 12),
 $-(CH_2)_n-O-, m-$ or $p-C_6H_4-O-CH(CH_3)_2-$

30 (n is an integer of 1 to 11),
 $-(CH_2)_n-O-, m-$ or $p-C_6H_4-C(O)O-(CH_2)_m-$
(m and n are integers of 1 to 12, however, $2 \leq m + n \leq 13$),
 $-(CH_2)_n-OC(O)-O-, m-$ or $p-C_6H_4-C(O)O-(CH_2)_m-$
(m and n are integers of 1 to 11, however, $2 \leq m + n \leq 12$),
35 $-(CH_2)_n-O-, m-$ or $p-C_6H_4-OC(O)-(CH_2)_m-$,

(m and n are integers of 1 to 12, however, $2 \leq m + n \leq 13$),
 $-(CH_2)_n-C(O)O-o-, m-$ or $p-C_6H_4-(CH_2)_m-$,

(m and n are integers of 1 to 11, however, $2 \leq m + n \leq 12$),
and the like.

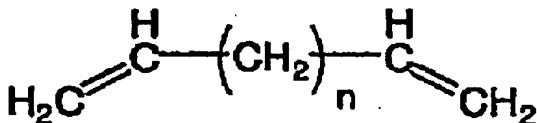
5 [0050]

R^8 is a hydrogen atom or a methyl group, but preferably a hydrogen atom. When R^7 is an alkyl group having 1 to 20 carbon atoms, its structure is not particularly restricted, but there may be mentioned the following.

10 [0051]

[Chemical 10]

15



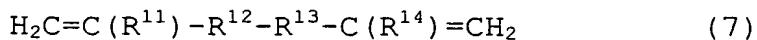
[0052]

From the availability viewpoint of raw materials, n is preferably 2, 4 or 6.

A compound containing two alkenyl groups represented by
20 the general formula 5 is preferably added in an excess amount during or at a terminal stage of living radical polymerization. The terminal stage of polymerization is a point at which preferably not less than 80% and more preferably not less than 90% of monomers are reacted.

25 <Alkenyl-containing monomer>

The polymer (I) can also be produced by adding a compound having both an alkenyl group with high polymerizability and an alkenyl group with low polymerizability during or after completion of the living radical polymerization. The compound
30 having both a polymerizable alkenyl group and an alkenyl group low in polymerizability is not particularly restricted, but there may be mentioned compounds represented by the general formula 7;



35 (wherein R^{11} and R^{14} represent hydrogen or methyl, R^{12} represents

$-\text{C}(\text{O})\text{O}-$ (ester group) or ortho-, meta- or para-phenylene group and R^{13} represents a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally have one or more ether bonds).

5 A polymer is produced by living radical polymerization, and further the above-mentioned compound having both a polymerizable alkenyl group and at least one alkenyl group other than that is reacted as the second monomer. In living radical polymerization, the polymerization terminus has the
10 polymerization activity, thus when a vinyl monomer is newly added, polymerization proceeds again. Therefore, when the vinyl monomer having both a polymerizable alkenyl group and at least one alkenyl group other than that is added, radical addition reaction occur in the alkenyl group site with
15 polymerization activity. Then, the other alkenyl group remains unreacted, so that an alkenyl-terminated polymer is obtained. Such second monomer may be newly reacted by adding with a catalyst after completion of the first polymerization and then isolating the polymer, or may be reacted by adding
20 during the polymerization (in-situ). In the latter case, the higher the monomer conversion rate of the first polymerization is, the more preferable it is. It is preferably not less than 80%. If it is not more than 80%, an alkenyl group distributes not in the molecular terminus but in the side chain, thereby
25 mechanical property of the cured product is deteriorated.

[0053]

 In this case, when such compound comprising both a polymerizable alkenyl group and at least one alkenyl group other than that is added in an equal amount to the number of the
30 polymerization terminus (since it is living polymerization, almost equal to the number of initiation site of the initiator), in principle, to all the terminus, one alkenyl group is to be introduced. However, for surely introducing an alkenyl group to the entire terminus, an excess amount, specifically 1 to 5
35 equivalent amount of the compound is preferably used. When more

than 5 equivalent amount of the compound is used, an alkenyl group is introduced to a terminus of the polymer in high density, it is not preferable in view of cured product physical property. [0054]

5 In the above general formula 7, one containing an ester group as R^{12} is a (meth)acrylate compound, and one containing a phenylene group as R^{12} is a styrenic compound. As R^{13} in the general formula 7, there may be mentioned alkylene groups such as methylene, ethylene and propylene; o-, m- or p-phenylene group; aralkyl groups such as benzyl; and alkylene groups containing an ether bond, such as $-CH_2CH_2-O-CH_2-$ and $-O-CH_2-$.
10 [0055]

Among these, the following compounds are preferred because of their ready availability.

15 $H_2C=C(H)C(O)O(CH_2)_n-CH=CH_2$, $H_2C=C(CH_3)C(O)O(CH_2)_n-CH=CH_2$,
(in each formula, n represents an integer of 0 to 20);
 $H_2C=C(H)C(O)O(CH_2)_n-O-(CH_2)_mCH=CH_2$,
 $H_2C=C(CH_3)C(O)O(CH_2)_n-O-(CH_2)_mCH=CH_2$,
(in each formula, n represents an integer of 0 to 20, and m
20 represents an integer 0 to 20);
o-, m-, p-divinylbenzene,
o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH=CH_2$,
o-, m-, p- $H_2C=CH-C_6H_4-CH_2-C(CH_3)=CH_2$,
o-, m-, p- $H_2C=CH-C_6H_4-CH_2CH_2CH=CH_2$,
25 o-, m-, p- $H_2C=CH-C_6H_4-OCH_2CH=CH_2$,
o-, m-, p- $H_2C=CH-C_6H_4-OCH_2-C(CH_3)=CH_2$,
o-, m-, p- $H_2C=CH-C_6H_4-OCH_2CH_2CH=CH_2$,
o-, m-, p- $H_2C=C(CH_3)-C_6H_4-C(CH_3)=CH_2$,
o-, m-, p- $H_2C=C(CH_3)-C_6H_4-CH_2CH=CH_2$,
30 o-, m-, p- $H_2C=C(CH_3)-C_6H_4-CH_2C(CH_3)=CH_2$,
o-, m-, p- $H_2C=C(CH_3)-C_6H_4-CH_2CH_2CH=CH_2$,
o-, m-, p- $H_2C=C(CH_3)-C_6H_4-OCH_2CH=CH_2$,
o-, m-, p- $H_2C=C(CH_3)-C_6H_4-OCH_2-C(CH_3)=CH_2$,
o-, m-, p- $H_2C=C(CH_3)-C_6H_4-OCH_2CH_2CH=CH_2$,
35 (in the above formulas, C_6H_4 denotes a phenylene group).

Production of a block copolymer

In the present invention, a block copolymer is produced by adding the above-mentioned polymer (I) to a living radical polymerization system.

5 [0056]

As conditions of this living radical polymerization, the same as those described for the production of the polymer (I) can be preferably used.

<Monomer>

10 As a monomer to be used in the living radical polymerization, the same as those described for the production of the polymer (I) can be preferably used. Those may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from 15 the viewpoint of physical properties of the products. More preferred are acrylic acid ester monomers and methacrylic acid ester monomers, and still more preferred are butyl acrylate monomers. In the practice of the present invention, such a preferred monomer may be copolymerized with some other monomers 20 and, on that occasion, the content of such preferred monomer is preferably 40% on the weight basis. The term (meth)acrylic acid employed hereinabove means acrylic acid and/or methacrylic acid.

<Initiator>

25 As an initiator to be used in the living radical polymerization, and particularly for the atom transfer radical polymerization, the same as those described for the production of the polymer (I) can be preferably used.

<Catalyst>

30 As a catalyst to be used in the living radical polymerization, and particularly for the atom transfer radical polymerization, the same as those described for the production of the polymer (I) can be preferably used.

<Polymerization conditions>

35 As polymerization conditions such as a solvent and

temperature for carrying out the living radical polymerization, and particularly the atom transfer radical polymerization, the same as those described for the production of the polymer (I) can be preferably used.

5 <Addition of polymer (I)>

The time for adding the polymer (I) to the living radical polymerization system is not particularly restricted but is preferably in the terminal stage of polymerization. According to the production method employed, the polymer (I) may have a 10 group which is to be an initiator of living radical polymerization. For example, there can be mentioned the case with the atom transfer radical polymerization using an allyl halide as an initiator to produce the polymer (I). In that case, it is possible that living radical polymerization starts again 15 from that site. Also in cases where such is to be avoided, the addition should preferably be made at the final stage of polymerization where the monomer remains little.

[0057]

The amount of the polymer (I) to be added is not 20 particularly restricted but is preferably such that the number of growing termini in living radical polymerization be equal to the number of the terminus represented by the general formula 1 in polymer (I).

The polymer (I) may be added as such or in the form of 25 a solution in a solvent which will not adversely affect the living radical polymerization.

Structure of the block copolymer

The structure of the block copolymer of the present invention is not particularly restricted but includes those 30 copolymers classifiable on the basis of polymer (I) and of the system to which the polymer (I) is added, namely living radical polymerization, as follows:

(1) living radical polymerization using a polymer (I) having one group represented by the general formula 1 per 35 molecule and a unifunctional initiator; (2) living radical

polymerization using a polymer (I) having one group represented by the general formula 1 per molecule and a bifunctional initiator; (3) living radical polymerization using a polymer (I) having one group represented by the general formula 1 per 5 molecule and a polyfunctional initiator; (4) living radical polymerization using a polymer (I) having two groups represented by the general formula 1 per molecule and a unifunctional initiator; (5) living radical polymerization using a polymer (I) having more than two groups represented by 10 the general formula 1 per molecule and a unifunctional initiator; (6) living radical polymerization using a polymer (I) having two groups represented by the general formula 1 per molecule and a bifunctional initiator; (7) living radical polymerization using a polymer (I) having a plurality of groups 15 represented by the general formula 1 per molecule and a multifunctional initiator; and so forth.

In the case of (1), an AB type block copolymer is obtained; in the case of (2) or (4), an ABA type block copolymer is obtained; in the case of (3) or (5), a stellar block copolymer 20 is obtained; in the case of (6), a multiblock copolymer is obtained; and in the case of (7), a crosslinked block copolymer is obtained.

[0058]

For each polymer block, various species can be 25 synthesized. In an ABA type block copolymer, for instance, when A is a polymer having a higher glass transition point (not specifically restricted but, for example, not lower than 25°C) and B is a polymer having a lower glass transition point (not specifically restricted but, for example, not higher than 25°C), 30 properties as a thermoplastic elastomer can be expected. In the case of stellar polymers as well, properties as a thermoplastic elastomer can be expected when a polymer block having a higher glass transition point is used as the exterior block and a polymer block having a lower glass transition point 35 as the inside block.

[0059]

Accordingly, by the present invention, block copolymers in which various species of blocks are combined in various orders can be obtained, and can be used in various fields such 5 as thermoplastic elastomers and impact resistance improving agents.

Uses

<Thermoplastic elastomer>

The block copolymer obtained by the production method of 10 the present invention can be used in substantially the same fields of application as the existing styrenic elastomers. More specifically, it can be used for modifying resins or asphalt, for preparing compounds of the block copolymer with resins (with a plasticizer, a filler, a stabilizer, etc. added 15 as occasion demands), as an antishrink agent for thermosetting resins, or as a base polymer for adhesives or pressure-sensitive adhesives or for damping materials. As specific fields of application, there may be mentioned automotive upholstery and exterior, electric and electronic fields, food wrapping films 20 and tubes, drug containers or containers for medical use, sealable articles and the like.

<Impact resistance improving agent>

While the block copolymer obtained by the production method of the present invention by itself can serve as a molding 25 material as a resin having impact resistance, it can serve as an impact resistance improving agent as well for providing various thermoplastic resins and thermosetting resins with a high level of impact resistance when admixed with said resins. Further, it can also be used as a processability improving agent, 30 compatibilizing agent, flattening agent, heat resistance modifier or the like. Furthermore, improvement of gas barrier property based on an isobutylene polymer can be expected.

[0060]

The thermoplastic resins which can be improved in shock 35 resistance by addition of the block copolymer of the present

invention include, but are not limited to, polymethyl methacrylate resins, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins, polycarbonate resins, polyester resins, polycarbonate resin-polyester resin blends, homopolymers and copolymers obtained by polymerizing 70 to 100% by weight of at least one vinyl monomer selected from the group consisting of aromatic alkenyl compounds, vinyl cyanide compounds and (meth)acrylic acid esters and 0 to 30% by weight of another vinyl monomer copolymerizable therewith, such as ethylene, propylene or vinyl acetate and/or a copolymerizable conjugated diene monomer, such as butadiene or isoprene, polystyrene resins, polyphenylene ether resins, polystyrene-polyphenylene ether resin blends and the like. Said block copolymer can be used in a wide variety of thermoplastic resins. In particular, polymethyl methacrylate resins, polyvinyl chloride resins, polypropylene resins, cyclic polyolefin resins, polycarbonate resins and polyester resins, among others, are preferred since they can readily show its characteristics such as improved weathering resistance and impact resistance.

[0061]

As the method of adding the block copolymer of the present invention to various resins, there may be mentioned the method comprising mechanically mixing and shaping into pellets using a conventional apparatus such as a Banbury mixer, roll mill or twin-screw extruder. The pellets shaped by extrusion can be molded in a wide temperature range and, for molding, an ordinary injection molding machine, blow molding machine or extrusion molding machine, for instance, is used.

[0062]

Furthermore, in the resulting resin compositions, there may be incorporated one or more additives as necessary, including impact resistance improving agents, stabilizers, plasticizers, lubricants, flame retardants, pigments, fillers and the like. More specifically, there may be mentioned impact

resistance improving agents such as methyl methacrylate-butadiene-styrene copolymers (MBS resins), acrylic graft copolymers and acrylic-silicone composite rubber type graft copolymers; stabilizers such as triphenyl phosphite; 5 lubricants such as polyethylene wax and polypropylene wax; fire retardants such as phosphate fire retardants, e.g. triphenyl phosphate, tricresyl phosphate, bromine-containing fire retardants, e.g. decarbromobiphenyl, decabromodiphenyl ether, and antimony trioxide; pigments such as titanium oxide, zinc 10 sulfide and zinc oxide; and filler such as glass fiber, asbestos, wollastonite, mica, talc and calcium carbonate.

[0063]

[Effect of the Invention]

By adding, according to the present invention, various 15 alkenyl-terminated polymers to a polymerization system for living radical polymerization, it is possible to obtain, with ease, block copolymers resulting from binding of these polymers to one another. Furthermore, by producing the polymer to be added by controlled radical polymerization, further by living 20 radical polymerization, block copolymers well controlled in the molecular weight of the polymer block to be bound can be obtained.

25

30

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[Document Name] Abstract

[Abstract]

[Subject] The present invention has for its subject to provide a method of easily producing a block copolymer composed of any of various polymers and a living radical polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

[Means for Solving] In the present invention, a block copolymer can be produced easily by adding a polymer (I) containing an alkenyl group in at least one terminus to a living radical polymerization system. Furthermore, said polymer (I) is produced by using controlled radical polymerization, preferably by living radical polymerization, and still more preferably by atom transfer radical polymerization while easily being well controlled in the molecular weight. As the result, a block copolymer well controlled in the molecular weight of the polymer block to be bound can be obtained.

[Selective Figure] none